

PROCESS FOR UPGRADING AN OLIGOMERIZATION PRODUCT

The present invention relates to a process for upgrading an oligomerization product. More particularly, the invention relates to a process for upgrading an oligomerization product through catalytic hydrotreating to yield an upgraded oligomerization product with improved pour point, and increased viscosity index.

Background of the Invention

Preparation of base oil stocks by hydrocracking, dewaxing, and hydrotreating is well known in the art. Generally, mineral oil based hydrocarbon feedstocks with paraffinic content are dewaxed to remove the easily solidified paraffins. Dewaxing may be generally accomplished through two methods. The first method involves hydrocracking in the presence of shape selective catalysts capable of selectively cracking n-paraffins and iso-paraffins. Commonly used shape selective catalysts for hydrocracking are

crystalline aluminosilicates optionally associated with a hydrogenating metal.

Typical conditions for catalytic hydrocracking include a temperature between 290°C and 450°C and hydrogen partial pressure of 250-1500 psig. Dewaxing may also be performed through solvent dewaxing using refrigeration to crystallize the paraffinic portion of the feed and using a solvent, such as methyl-ethyl-ketone, to sufficiently dilute the oil portion permitting rapid filtration to separate the wax from the oil. Dewaxing is further described by J. Gary and G. Handwerk in Petroleum Refining Technology and Economics, 1984, 2nd ed., p. 241-245, which is incorporated by reference herein.

Hydrotreating is typically done following catalytic dewaxing to saturate olefinic by-products of the dewaxing process, improve stability, and reduce sulfur content. Hydrotreating processes are described in U.S. Patents 4,267,071 and 4,600,503, which are incorporated by reference herein.

While the purpose of the above mentioned processes is to produce a lubricating base oil with improved stability, pour point, and viscosity index, it is widely believed in the industry that certain levels of oxidative and thermal stability in lubricant oils can only be obtained by using full synthetic formulations as opposed to mineral oil based lubricants. Oxidative stability refers to the ability of the oil to resist oxidation, which generally leads to deterioration of the oil. The belief in the superiority of synthetics has lead to an

increasing demand in the industry for high performance, high viscosity index synthetic base oils with high oxidative stability and low pour point. Currently, poly-alpha-olefins (PAOs) are commonly used as synthetic base oils. PAOs are typically produced through the polymerization of 1-alkenes using a Lewis acid, such as AlCl₃ or BF₃, or Ziegler-catalysts. Their preparation and properties are described by J. Brennan in Ind. Eng. Chem. Prod. Res. Dev. 1980, 19, p. 2-6, which is incorporated herein by reference. PAOs are also described in U.S. Patent 3,742,082, which is incorporated herein by reference. PAOs provide low temperature fluidity (e.g. low pour point), high viscosity index and high oxidative stability; however, PAOs also have a high manufacture price, generally associated with the expense of the 1-alkene feedstock required for PAO production.

This has created a demand for a low cost alternative to PAOs, such as a process for making synthetic base oils from oligomerization products. U.S. Patent 4,650,917, for example, discloses a method for enhancing the viscosity index of a synthetic lubestock by contacting the synthetic lubestock with a solid acidic catalyst, such as an acidic zeolite, under isomerization conditions, then separating out the high viscosity index fraction through sorbing by a shape-selective zeolite, followed by desorbing. Viscosity index is an important characteristic of lubricants because it provides a measure of how

much the viscosity of the lubricant changes with temperature. High viscosity index, which indicates a relatively lower rate of viscosity change with temperature, is generally desired. Viscosity index is typically higher in paraffinic stocks, especially paraffinic stocks with minimal branching. This raises a problem, however, because such paraffinic stocks also typically have high pour points, an undesirable quality. Therefore, development of a process for improving the viscosity index and pour point of an oligomerization product for use as a synthetic base oil would be a significant contribution to the art and to the economy.

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Brief Summary of the Invention

It is thus an object of this invention to provide an improved process for upgrading an oligomerization product through catalytic hydrotreating of the oligomerization product.

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It is a further object of this invention to provide a novel catalyst system effective for upgrading an oligomerization product through catalytic hydrotreating.

It is still another object of this invention to employ this novel catalyst system as a catalyst in the upgrading of an oligomerization product through catalytic hydrotreating.

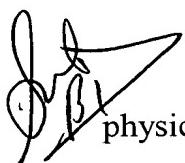
The present invention provides a process for upgrading an oligomerization product through catalytic hydrotreating by contact with a composition comprising platinum and a ZSM-5 zeolite, thereby forming an upgraded oligomerization product (a synthetic base oil). The oligomerization product can be an oligomer of an olefin, a co-oligomer of two different olefins or a ter-oligomer of three different olefins. The upgrading process results in an upgraded oligomerization product that exhibits at least one of the following improvements over the oligomerization product:

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lower pour point as determined using test method ASTM D97;

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higher viscosity index as determined using test method ASTM D567.



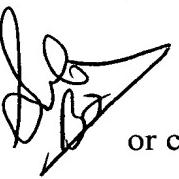
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Further, the upgrading process results in a product that exhibits physical characteristics making it desirable for use as a synthetic base oil. Such physical characteristics include, but are not limited to, a pour point that is less than about -20°C and a viscosity index that is greater than about 100. These values for pour point and viscosity index are representative of commercially acceptable values for a lube base oil.

Other objects and advantages will become apparent from the detailed description and the appended claims.

Detailed Description of the Invention

The oligomerization product to be upgraded according to the present invention comprises oligomeric olefins. Each of the olefins, as they exist in their state prior to oligomerization to form the oligomerization product, typically contain at least 2 and less than 16 carbon atoms per molecule. More typically, each of the olefins, prior to oligomerization, contain at least 2 and less than 10 carbon atoms per molecule; and most typically, each of the olefins, prior to oligomerization, contain at least 2 and less than 5 carbon atoms per molecule. Oligomerization of the olefin units can be carried out by any commonly used method. Because methods of oligomerization are well known to those skilled in the art, a description of such a method of oligomerization is omitted herein for the interest of brevity. Such methods of oligomerization are described in U.S. Patents 5,942,642 and 4,526,950, which are incorporated by reference herein.

15  The oligomerization product can comprise, consist essentially of, or consist of at least one oligomer of an olefin formed by any commonly used method of oligomerization. Alternately, the oligomerization product can comprise, consist essentially of, or consist of a co-oligomer of a first olefin and a second olefin formed by any commonly used method of co-oligomerization.

20 Alternately, the oligomerization product can comprise, consist essentially of, or

consist of a ter-oligomer of a first olefin, a second olefin, and a third olefin formed by any commonly used method of ter-oligomerization. Further, the oligomerization product can comprise, consist essentially of, or consist of one or more mixtures of an oligomer, co-oligomer, and ter-oligomer. Examples of suitable olefins for use in oligomerization, co-oligomerization, or ter-oligomerization include but are not limited to: ethene, propene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, tridecene, tetradecene, pentadecene, and any and all straight-chain (n-) and branched-chain (iso-) isomers and isomeric mixtures thereof.

Upgrading of the oligomerization product takes place by catalytic hydrotreating of the oligomerization product through contact with a catalyst system comprising, consisting of, or consisting essentially of a group VIII metal component and a ZSM-5 zeolite under conversion conditions. The term "metal" used herein also includes a compound of the metal.

Catalytic hydrotreating, as used herein, includes selective/minor cracking, isomerization and hydrogenation.

The group VIII metal employed in the present invention can be incorporated into the ZSM-5 zeolite by any suitable method known to one skilled in the art such as ion exchange or impregnation. The group VIII metal can be present in the catalyst system in any amount that is catalytically effective

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to facilitate hydrogenation. Generally, the amount of group VIII metal present in the catalyst system is in the range of from about 0.1 to about 2.0 weight %, preferably in the range of from about 0.2 to about 1.0 weight %, and most preferably in the range of from 0.2 to 0.8 weight % based on the total weight of the catalyst system, measured on an elemental group VIII metal basis. Any group VIII metal with hydrogenating ability can be used, including iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. The particularly preferred group VIII metal in the present invention is platinum.

The ZSM-5 zeolite useful in the present invention generally has a
silica/alumina ratio in the range of from about 20 to about 400; more preferably
from about 20 to about 200; and most preferably from 30 to 100. U.S. Patent
3,702,886 includes a description concerning preparation of ZSM-5 and is
incorporated herein by reference. The ZSM-5 zeolite can be used in its alkali
metal form, however, for the purposes of the present invention, it is preferred
that the ZSM-5 zeolite be in the acidic (hydrogen) form, which can be
accomplished by any suitable method known to one skilled in the art.
Examples of suitable methods to convert a zeolite to its hydrogen form include
acid treatment, where the zeolite is treated with a strong acid (such as HCl); or
ion-exchange, where the zeolite is treated with a strong base (such as NH₃),

thereby forming an ammonium intermediate followed by calcination of the ammonium intermediate to yield the hydrogen form.

Generally, the amount of zeolite present in the catalyst system is in the range of from about 50 to about 99 weight %, preferably in the range of from about 60 to about 95 weight %, and most preferably in the range of from 5
70 to 90 weight %, based on the total weight of the catalyst system.

Reaction conditions for catalytic hydrotreating of the oligomerization product can include hydrogen pressure in the range of from about 0 to about 2000 psig; more preferably from about 50 to about 1500 psig; and most preferably from 150 to 1000 psig, and can also include a temperature in the range of from about 180°C to about 400°C; more preferably from about 10
190°C to about 350°C; and most preferably from 200°C to 300°C.

Contacting the oligomerization product with the catalyst system can be carried out in any technically suitable manner, in a batch or semi-15 continuous or continuous process, and under a condition effective to upgrade the oligomerization product. Generally, the oligomerization product may be introduced into a reactor having a fixed catalyst bed, or a moving catalyst bed, or a fluidized catalyst bed, or combinations of any two or more thereof by any means known to one skilled in the art.

While a temperature in excess of about 240°C is generally not recommended, as such an increase in temperature tends to promote deep/severe hydrocracking (which is specifically sought to be avoided here), a somewhat higher temperature can be effective for further reducing the pour point of the oligomerization product.

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The following examples are provided to further illustrate this invention and are not to be considered as unduly limiting the scope of this invention.

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This example details the preparation and/or nature of catalysts which were subsequently tested as catalysts in the upgrading of an oligomerization product to produce a synthetic lube base stock.

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Catalyst A (control)
A commercially available Ni/Al₂O₃ catalyst manufactured by UCI (Louisville, KY) under product designation C38 containing 20 weight % nickel.

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Catalyst B (control)
A 56.3 gram quantity of an alumina bound SAPO-11 was extruded into 1/16" extrudates and calcined at 538°C for 3 hours (the SAPO-11 was manufactured by UOP LLC, DesPlaines, IL). The calcined SAPO-11/Al₂O₃ was impregnated, by incipient wetness, with 25.2 grams of an

aqueous solution containing 2.0 wt. % H₂PtCl₆ and 2.0 wt. % citric acid. The thus obtained impregnated SAPO-11/Al₂O₃ was calcined in air at 538°C for 6 hours followed by heating in the presence of hydrogen at 400°C for 2 hours. The resulting catalyst contained 0.34 wt. % Pt.

5 ***Catalyst C (control)***

A 35.1 gram quantity of an alumina bound Mordenite molecular sieve, MOR/Al₂O₃ was extruded into 1/16" extrudates and calcined at 538°C for 1 hour (the Mordenite molecular sieve was manufactured by Zeolyst, under product designation CVB-20A). The calcined MOR/Al₂O₃ was impregnated, by incipient wetness, with 17.5 grams of an aqueous solution containing 2.0 wt. % H₂PtCl₆ and 2.0 wt. % citric acid. The thus obtained impregnated MOR/Al₂O₃ was calcined in air at 538°C for 6 hours followed by heating in the presence of hydrogen at 400°C for 2 hours. The resulting catalyst contained 0.38 wt. % Pt.

15 ***Catalyst D (control)***

A 35.9 gram quantity of an alumina bound Beta molecular sieve , BEA /Al₂O₃, was extruded into 1/16" extrudates and calcined at 538°C for 1 hour (the Beta molecular sieve was manufactured by UOP LLC, DesPlaines, IL, under product designation Beta-Zeolite). The calcined BEA/Al₂O₃ was impregnated, by incipient wetness, with 23.3 grams of an aqueous solution

containing 2.0 wt. % H₂PtCl₆ and 2.0 wt. % citric acid. The thus obtained impregnated BEA/Al₂O₃ was calcined in air at 538°C for 6 hours followed by heating in the presence of hydrogen at 400°C for 2 hours. The resulting catalyst contained 0.50 wt. % Pt.

5 ***Catalyst E (inventive)***

A 14.1 gram quantity of an alumina bound H ZSM-5 was extruded into 1/16" extrudates and calcined at 538°C for 2 hours (the H ZSM-5 was manufactured by UCI, Louisville, KY, under product designation T-4480). The calcined H ZSM-5/Al₂O₃ was impregnated, by incipient wetness, with 7.4 grams of an aqueous solution containing 2.0 wt. % H₂PtCl₆ and 2.0 wt. % citric acid. The thus obtained impregnated H ZSM-5/Al₂O₃ was calcined in air at 538°C for 6 hours. The resulting catalyst contained 0.44 wt. % Pt.

10 ***Example II***

This example illustrates the use of the catalysts described in Example I as catalysts in the upgrading of an oligomerization product to provide improved pour point and increased viscosity index. In all runs, the oligomerization product used for upgrading was an ethylene/propylene co-oligomer produced through co-oligomerization via a Cp₂ZrCl₂-MAO catalyst obtained from Aldrich Chemical Co.. Cp₂ZrCl₂ is Bis(cyclopentadiene) zirconium dichloride (Zirconocene) and MAO is methylaluminoxane. The

resultant oligomer, prior to upgrading, was quenched with a 10% mixture of HCl in MeOH, washed with water, dried, filtered, and evaporated.

In run 1, a 20 ml sample of catalyst A, described in Example I, was placed into a stainless steel tube reactor (length: about 18 inches; inner diameter: about 0.5 inch). The oligomerization product, as described above, was passed downwardly through the reactor at a flow rate of about 40 ml/hour, at a temperature of about 220°C, and at a pressure of about 500 psig.

Additionally, hydrogen gas was added to the reactor at a rate of about 480 ml/minute. The upgraded product exited the reactor tube and was collected and cooled. The product sample was tested for pour point according to test method ASTM D97 and for viscosity index according to test method ASTM D567.

Test data results are summarized in the Table.

In run 2, a 10 ml sample of catalyst B, described in Example I, was placed into a stainless steel tube reactor (length: about 18 inches; inner diameter: about 0.5 inch). The oligomerization product, as described above, was passed downwardly through the reactor at a flow rate of about 30 ml/hour, at a temperature of about 300°C, and at a pressure of about 500 psig.

Additionally, hydrogen gas was added to the reactor at a rate of about 360 ml/minute. The upgraded product exited the reactor tube and was collected and cooled. The product sample was tested for pour point according to test method

ASTM D97 and for viscosity index according to test method ASTM D567.

Test data results are summarized in the Table.

In run 3, a 10 ml sample of catalyst B, described in Example I,
was placed into a stainless steel tube reactor (length: about 18 inches; inner
diameter: about 0.5 inch). The oligomerization product, as described above,
was passed downwardly through the reactor at a flow rate of about 30 ml/hour,
at a temperature of about 250°C, and at a pressure of about 500 psig.

Additionally, hydrogen gas was added to the reactor at a rate of about 360
ml/minute. The upgraded product exited the reactor tube and was collected and
cooled. The product sample was tested for pour point according to test method
ASTM D97 and for viscosity index according to test method ASTM D567.

Test data results are summarized in the Table.

In run 4, a 10 ml sample of catalyst C, described in Example I,
was placed into a stainless steel tube reactor (length: about 18 inches; inner
diameter: about 0.5 inch). The oligomerization product, as described above,
was passed downwardly through the reactor at a flow rate of about 30 ml/hour,
at a temperature of about 250°C, and at a pressure of about 500 psig.

Additionally, hydrogen gas was added to the reactor at a rate of about 360
ml/minute. The upgraded product exited the reactor tube and was collected and
cooled. The product sample was tested for pour point according to test method

ASTM D97 and for viscosity index according to test method ASTM D567.

Test data results are summarized in the Table.

In run 5, a 10 ml sample of catalyst D, described in Example I,
was placed into a stainless steel tube reactor (length: about 18 inches; inner
diameter: about 0.5 inch). The oligomerization product, as described above,
was passed downwardly through the reactor at a flow rate of about 30 ml/hour,
at a temperature of about 220°C, and at a pressure of about 500 psig.

5 Additionally, hydrogen gas was added to the reactor at a rate of about 360
ml/minute. The upgraded product exited the reactor tube and was collected and
cooled. The product sample was tested for pour point according to test method
10 ASTM D97 and for viscosity index according to test method ASTM D567.

Test data results are summarized in the Table.

In inventive run 6, a 10 ml sample of catalyst E, described in
Example I, was placed into a stainless steel tube reactor (length: about 18
15 inches; inner diameter: about 0.5 inch). The oligomerization product, as
described above, was passed downwardly through the reactor at a flow rate of
about 30 ml/hour, at a temperature of about 220°C, and at a pressure of about
500 psig. Additionally, hydrogen gas was added to the reactor at a rate of about
360 ml/minute. The upgraded product exited the reactor tube and was collected
20 and cooled. The product sample was tested for pour point according to test

method ASTM D97 and for viscosity index according to test method ASTM D567. Test data results are summarized in the Table.

Table 1					
	Run	Catalyst	Temp. (°C)	Pour point (°C)	Viscosity Index
5	1 (control)	A	220	-44.1	145
10	2 (control)	B	300	-38.9	148
	3 (control)	B	250	-35.0	150
	4 (control)	C	250	-41.4	148
	5 (control)	D	220	-35.6	151
	6 (inventive)	E	220	-47.3	152
					700° F ⁺
					wt.% yield Σ

Wt. % yield Σ 700° F⁺ represents a summation of the weight percents of all the compounds present in the product with boiling points equal to and in excess of 700°F.

15 The test data presented in the Table show that the use of Pt/HZSM-5 in inventive Run 6 produced an overall superior upgraded oligomerization product, in terms of pour point, viscosity index and wt. % yield, as compared to control Runs 1 - 5. The upgraded oligomerization product of inventive Run 6, as compared to control Runs 1 - 5, demonstrated: a decrease in pour point in the range of from about 7% to about 35%; an increase

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in viscosity index in the range of from about 0.7 % to about 5%; and a higher wt. % yield $\Sigma 700^{\circ}\text{F}+$ as compared to the control Runs with the exception of control Run 3, which demonstrated an increase in wt. % yield $\Sigma 700^{\circ}\text{F}+$ of 3.8% over inventive Run 6. However, the pour point of control Run 3 was 26% higher and the viscosity index of control Run 3 was 1.3% lower than that of inventive Run 6.

Reasonable variations, modifications, and adaptations can be made within the scope of the disclosure and the appended claims without departing from the scope of this invention.